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Transient Voltage Changes Produced in Corroding Metals and Alloys

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The formation of "hollow whiskers" by the action of slightly acidified potassium ferricyanide and ferrocyanide solutions on metals and alloys (1) appeared to indicate that corroding metals produce bursts of metal ions from various point anodes. Since these bursts of ions appeared to be of a sporadic nature, it seemed possible that there might be transient fluctuations of the electrical charge on the metal. The present communication reports on the detection of such fluctuations in electrical charge.

The circuit shown in Fig. 1 was used. The voltmeter was of the high impedance type (11 megohms) with a chopper stabilized circuit. The electrodes consisted of an inert auxiliary electrode of platinum foil (1 x 4.5 cm) connected to a platinum wire and the test electrode, whose corrosion was to be studied. Various strips of metals and alloys were used as the test electrode. The cell and electrodes were placed in a grounded copper-jacketed chamber to control the temperature and provide a shield from stray currents. The corroding metals or alloys investigated were aluminum, aluminum alloys (2025 and 7075), magnesium ribbon, iron, mild steel (1010), and zinc, and each exhibited voltage fluctuations whose frequency and amplitude depended on the metal being studied. The fluctuations from pure aluminum, the two aluminum alloys, and magnesium were generally extremely rapid (1 to 2 or more per sec) and greater than 100 μ V in amplitude. Using a low input impedance audio amplifier with the platinum and the corroding electrode connected directly across the input, a wide range of fluctuations in the audio range could be heard with a loud speaker. Voltage fluctuations from corroding iron, steel, and zinc were slower (1 to 3 or less per 5-min. interval) and less in amplitude (<50 or 60 μ V). The fluctuations in the potential appeared to be directly related to the corrosion, because the addition of an inhibitor caused them to disappear. Likewise, a non-corroding metal (platinum) was studied (in this case both electrodes were platinum) no fluctuations were observed. As an example, Fig. 2 shows the voltage fluctuations in a 1010 mild steel coupon partly immersed in distilled water plus 0.1% NaCl and the effect of a corrosion inhibitor, sodium nitrite (2), in causing these fluctuations to disappear. Similar inhibitor effects were observed with aluminum in the presence of nitrates (3).

To account for these voltage fluctuations, it is postulated that they are caused by minute transient changes in the electrical charge on the electrode produced as a result of cathodic and anodic reactions during the corrosion process, the charge at any small interval of time representing the resultant charge of both reactions. The imbalance of charge may also be due to

transient changes in cathodic or anodic areas. If, for example, a corroding metal assumes a temporary increase in negative charge, the electrons would charge the plate of the capacitor in contact with it. An equal or opposite charge would develop on the other plate (flow of electrons away from the plate) thereby causing a difference in measurable potential across the resistance. The electrons might be expected to dissipate through the resistor to the platinum electrode and be removed as a result of reduction of the cations or neutral species in the solution. During a transient decrease in negative charge on the metal and capacitor plate, the flow of electrons would be from the platinum electrode, as a result of oxidation of the anions or neutral species in solution, to the other capacitor plate, again developing a measurable potential across the resistor. If no change in the charge occurs on the test electrode, no measurable potential is developed across the resistor. This is apparently the case for a noncorroding electrode such as platinum or a less noble metal in the presence of an inhibitor for the initial charge on the capacitor soon dissipates, and the measurable potential drops to zero. The time for the voltage developed across the resistor to decrease to zero appears to be directly related to the initial charge in the capacitor and the R.C. time constant and inversely related to the electrolyte concentration.

Investigations of these voltage fluctuations appear to offer much promise for the detection and study of the corrosion process and for the study of corrosion inhibitors. Thus far, these fluctuations give a qualitative "fingerprint" characterization of corrosion processes occurring in different metals and alloys. They also offer a very simple way to detect the efficacy of inhibitors, being able to detect corrosion instantane-

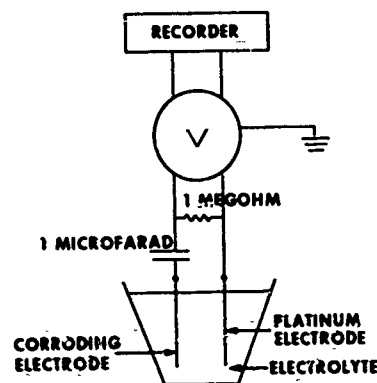


Fig. 1. Corrosion cell and circuit for detecting potential variations in corroding metals and alloys.

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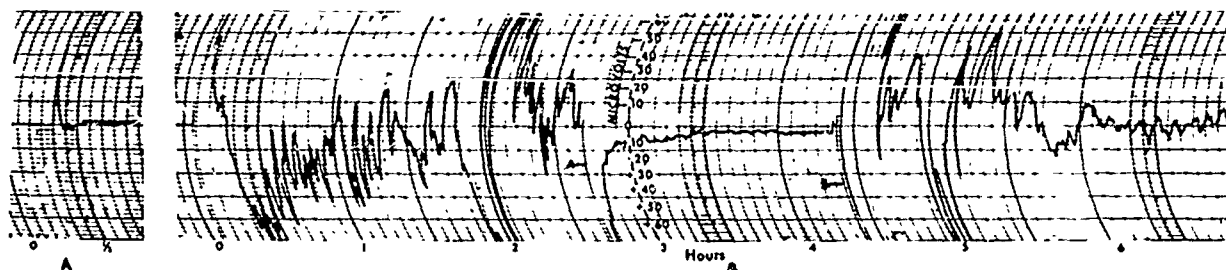


Fig. 2. Recorder trace of potential fluctuations. Chart speed 3 in/hr. A, Completely immersed platinum electrode (1 x 4.5 cm) in 0.1% NaCl solution; conductivity, 0.22 mhos; platinum electrode 1 cm from completely immersed auxiliary electrode, 25°C. B, Partially immersed (55 cm) 1010 steel electrode (1.3 x 18 cm) corroding in 0.1% NaCl solution; electrode 1 cm from completely immersed auxiliary electrode, 25°C. Chart A, electrodes transferred to fresh 0.1% NaCl solution plus 1% NaNO₂; Chart B, electrodes transferred to fresh 0.1% NaCl solution.

ously. Further analysis of the voltage fluctuations which is currently underway, will be required to relate them quantitatively to the corrosion rate and to determine the origin of the frequency and amplitude difference that differs with each metal.

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1968 JOURNAL.

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